Patent Claims

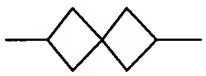
1. Process for the preparation of a compound of the general formula

$$R\text{-}(A^1\text{-}Z\text{-})_m\ B\text{-}CF_2O\text{-}A^2\text{-}(A^3)_n\text{-}R' \qquad (I)$$

in which

R is alkyl, in which one or more CH_2 groups may be replaced, independently of one another, by O, CF_2, CH=CH, CH=CF or CF=CF, with the proviso that peroxide structures O-O and formaldehyde acetals O-CH_2-O are excluded,

A^1 is, independently of one another, 1,4-cyclohexylene, 2,5-1,3-dioxanylene, 1,3-cyclobutylene or



A^2 and A^3 are 1,4-phenylene, in which, independently of one another, from one to four hydrogens may be replaced by fluorine or one or two CH groups may be replaced by N,

Z is a single bond, -CH_2-CH_2-, -CF_2-CF_2-, -CH=CH-, -CF=CF-, -CH=CF- or -CF=CH-,

B is 2,6-disubstituted naphthalene, 2,6-disubstituted 5,6,7,8-tetrahydronaphthalene or 2,6-disubstituted trans-decalin,

R' is R, F, OCF_3, OCF_2H, CF_3, Cl, SF_5, CN or NCS, and

m and n are, independently of one another, 0 or 1,

comprising the following steps:

a) conversion of a compound of the general formula

$$R\text{-}(A^1\text{-}Z\text{-})_mBX \quad (II),$$

in which X is halogen or =O and the other symbols are as defined in relation to the formula (I), into a carboxylic acid derivative with elimination of the group X and introduction of a C1 unit;

b) reaction of the carboxylic acid derivative with a phenol of the general formula

$$HO\text{-}A^2(\text{-}A^3)_n\text{-}R' \quad (III),$$

in which A^2, A^3, R' and n are as defined in relation to the formula (I), to give the compound of the formula (I).

2. Process according to Claim 1, characterised in that step a) is carried out as follows:

a') conversion of a compound of the general formula

$$R\text{-}(A^1\text{-}Z\text{-})_mBX \quad (II),$$

in which X is a halogen and the other symbols are as defined in relation to the formula (I), into the corresponding Grignard compound, reaction of the resultant Grignard compound with CO_2, and hydrolysis to the corresponding carboxylic acid of the formula

$$R\text{-}(A^1\text{-}Z\text{-})_mB\text{-}CO_2H \quad (IV)$$

or a salt thereof.

3. Process according to Claim 1 or 2, characterised in that X in the formula (II) is selected from the group consisting of Cl, Br and I and is particularly preferably Br.

4. Process according to one of Claims 1 to 3, characterised in that, for the preparation of the Grignard compound, a compound of the formula (II) in which B = 2,6-decalinyl, 2,6-tetrahydronaphthyl or 2,6-naphthyl is reacted with magnesium in a solvent which comprises at least one nonpolar solvent and at least one polar solvent, with external supply of heat.

5. Process according to one of Claims 1 to 4, characterised in that the reaction of the Grignard compound is carried out with gaseous CO_2.

6. Process according to one of Claims 1 to 5, characterised in that the esters are obtained from the acids (IV) and the phenols of the formula (III) $HO\text{-}A^2(\text{-}A^3)_n\text{-}R'$, in which A^2, A^3, R' and n are as defined in relation to the formula (I), by reaction under water-eliminating conditions.

7. Process according to one of Claims 1 to 6, characterised in that the ethers (I) are obtained from the esters by conversion into the bisalkylthionium salts (V) and reaction thereof with the phenol (III) in an oxidative fluorodesulfuration.

8. Process according to Claim 7, characterised in that the carboxylic acid (IV) is reacted with a preferably cyclic alkylthiol, in particular from the group consisting of ethanedithiol, propanedithiol and 1,2-benzenedithiol, to give the bisalkylthionium salt.

9. Process according to one of Claims 1 to 8, characterised in that the oxidant employed in the fluorodesulfuration is a compound which liberates halonium equivalents, preferably from the group consisting of dibromohydantoin, dimethyldibromohydantoin, N-bromo-succinimide, N-iodosuccinimide, 1,3-dibromo-5,5-dimethylhydantoin,

SO_2Cl_2, SO_2ClF, nitrosonium and nitronium salts, chloramine T and bromine, particularly preferably bromine.

10. Process according to one of Claims 1 to 9, characterised in that the fluorinating agent is selected from aliphatic and aromatic amine/hydrogen fluoride complexes, pyridine/hydrogen fluoride complexes, $NEt_3 \bullet 3HF$, 50% HF in pyridine, melamine•HF and polyvinylpyridine•HF.

11. Process according to one of Claims 1 to 10, characterised in that the ester is reacted with a fluorinating agent in the presence of an oxidant, preferably a brominating agent, to give the ethers (I) with formation of the thioesters as intermediates.

12. Process according to Claim 1, characterised in that step a) is carried out as follows:

a") conversion of a compound of the general formula

$$R\text{-}(A^1\text{-}Z\text{-})_mBX \quad (II),$$

in which X is an =O group, into a bis(alkylthio)carbenium salt by reaction with a suitable sulfur-containing compound.

13. Process according to Claim 12, characterised in that a ketene dithioketal is prepared by reaction of (II) with a 2-silyl-1,3-dithiane, which may be optionally substituted, preferably 2-trimethylsilyl-1,3-dithiane, in the presence of a deprotonating compound, preferably alkyllithium, particularly preferably n-butyllithium, and is subsequently converted into a bis(alkylthio)carbenium salt, preferably by acidification.

14. Process according to Claim 12 or 13, characterised in that the acid employed for the protonation is one of the general formula H^+Y^-, preferably trifluoromethanesulfonic acid or tetrafluoroboric acid/diethyl ether complex.

15. Process according to one of Claims 12 to 14, characterised in that the bis(alkylthio)carbenium salt has a non-coordinating or weakly coordinating anion, which is preferably selected from the group formed by tetrafluoroborate, hexafluorophosphate, perchlorate and perfluoroalkylsulfonate, in particular trifluoromethanesulfonate.

16. Process according to one of Claims 12 to 15, characterised in that the oxidant employed is a compound which liberates halonium equivalents, preferably dimethyldibromohydantoin, N-bromo-succinimide, N-iodosuccinimide, 1,3-dibromo-5,5-dimethylhydantoin, SO_2Cl_2, SO_2ClF, nitrosonium and nitronium salts, chloramine T or bromine, particularly preferably bromine.

17. Process according to one of Claims 12 to 16, characterised in that the fluorinating agent is selected from the group formed by aliphatic and aromatic amine/hydrogen fluoride complexes, pyridine/hydrogen fluoride complexes, $NEt_3 \bullet 3HF$, 50% HF in pyridine, melamine•HF and polyvinylpyridine•HF.